Morphology and Physical Properties of Injection-Molded, Mineral-Filled Polyamide 6/Poly(hydroxy ether of bisphenol A) Blends

G. GUERRICA-ECHEVARRíA, J. I. EGUIAZÁBAL, J. NAZÁBAL

Departamento de Ciencia y Tecnología de Polímeros, Facultad de Química,
UPV/EHU, P.O. Box 1072, 20080 San Sebastian, Spain

ABSTRACT: Polyamide 6 (PA 6)/poly(hydroxy ether of bisphenol A) (phenoxy) blends filled with up to 30% of both mica and calcium carbonate were obtained by extrusion and subsequent injection molding over the whole composition range. DSC and SEM showed the lack of influence of the fillers on the thermal properties and the morphology of the immiscible thermoplastic blends. The obtained positive effects of fillers on the Young's modulus and yield stress of the blends were, in many cases, larger than those observed in the pure components. The filler–presence-induced usual decrease in large-strain mechanical properties was smaller in the case of calcium carbonate than in the case of mica-filled blends. The shape of the inorganic particles, their adhesion level to the thermoplastic matrix, and the contact of the particles with the best performing component imposed by the large particle size, play probably the most important role in the physical properties. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1805–1814, 1999

Key words: polyamide 6; poly(hydroxy ether of bisphenol A); mineral filler; blends; morphology; mechanical properties

INTRODUCTION

There are two typical ways to modify the properties of a raw polymer. One is polymer blending, which is a low-cost technique that gives rise to new materials with tailored properties. The other is the addition of mineral fillers and fibers, which has been extensively used to modify such properties of thermoplastics as rigidity, strength, durability, and hardness. In the case of immiscible blends, control of the morphology is fundamental, hence, the influence of such parameters as processing conditions and composition, mainly on compatibility, has been studied.[1,2] In the case of filled polymers, the nature, shape, and size of the particles and their composition[3] are critical parameters that will determine the properties of the composite.

More complex, three-component systems, obtained by the addition of an inorganic filler to an immiscible blend have also been studied. In these cases, inorganic particles can be located solely within one polymeric phase, distributed between both polymeric components, or at the interphase. Immiscible blends with preferential distribution of particles between the components have been widely studied in the literature, including polypropylene (PP)/polycarbonate (PC) blends filled with talc,[4] PP/polyamide 6 (PA 6) blends filled with glass beads and fibers,[5] PP/PA 66 blends filled with glass beads,[6] poly(methyl methacrylate) (PMMA)/PP, polyethylene (PE)/PP, and PE/PMMA filled with carbon black,[7] PE/poly(ethylene vinyl acetate) filled with calcium carbonate,[8] or polyolefin/elastomer blends reinforced

---

with several fillers.[9–11] Other immiscible reinforced blends have been studied, such as short glass fiber-filled PP/PE blends,[12] talc-filled PP/LDPE blends,[13] PMMA/polystyrene (PS) blends filled with glass beads,[14] and poly vinyl fluoride (PVF)/PMMA and PVF/PS blends filled with sepiolite.[15]

Poly(ε-caprolactam) (PA 6) is a commonly used semicrystalline polyamide. Good mechanical properties and solvent resistance, usual in polyamides, have led to it's being blended with different polymeric materials, such as rubbers,[16] polyolefins, copolymers,[17,18] and other thermoplastics.[19–22] Several filled PA 6 have been commercialized. It has also been studied as a thermoplastic matrix for composites and has been reinforced with talc,[23] calcium carbonate, and silicate,[24] alumina and calcium phosphate,[25] or glass microspheres.[26] As mentioned, ternary systems PA 6/PP filled with glass fibers and beads have also been studied.[5,27,28]

Poly(hydroxyether of bisphenol A) (phenoxy) is a relatively tough and ductile thermoplastic with an excellent oxygen barrier property. It has a polar pendant group that is able to react with different polymers[29] and gives rise to several miscible[30–32] and immiscible blends.[33,34] Recent investigations[35] have demonstrated its good mechanical properties, including small-strain properties and ductility, attained in immiscible PA 6/phenoxy blends. Given the widespread use of filled nylons, the interest in the study of filled PA 6/phenoxy blends is clear.

This is why in this article, composites formed by a matrix of PA 6/phenoxy of different compositions, filled with up to 30% weight content with both mica and calcium carbonate, have been studied. The phase structure and morphology of the blends were studied by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) and the observed structure and morphology were related to the mechanical properties measured by means of tensile and impact tests.

EXPERIMENTAL

PA 6 (Durethan B30S, Bayer) had a molecular weight $M_w = 29,000$, determined by viscosimetry at 25°C in aqueous formic acid (85%), and the phenoxy (PKHH, Union Carbide) had an $M_w = 50,700$ and $M_n = 18,000$, determined by gelpermeation chromatography (GPC) in tetrahydrofuran (THF) at 30°C. The size distribution and composition of mica (dry-ground DG-10/20, Delta

Table I Chemical Composition and Size Distribution of Mica and Calcium Carbonate Particles

	Composition		Size Distribution	
Mica	SiO$_2$	48%	>32 μm:	0.5%
	Al$_2$O$_3$	34%	>20 μm:	8%
	K$_2$O	9.5%	>10 μm:	11%
	Others	8.5%	>5 μm:	45%
			<5 μm:	55%
Calcium carbonate	CaCO$_3$	99.0%	>44 μm:	0.05%
	MgCO$_3$	0.5%	>2 μm:	58%
	Others	0.5%	<2 μm:	42%

Tecnic, SA) and calcium carbonate (OMYACARB 2-BE, Clarianacal, SA, Zaragoza, Spain) are shown in Table I.

To obtain unfilled blends, both polymers were dried *in vacuo* at 80°C for 14 hours before processing to avoid moisture-induced degradation reactions, mixed at the desired weight ratios, and tumbled together before direct-injection molding (reciprocating screw BATTENFELD BA230E machine). The screw of the plasticization unit was a standard screw with a diameter of 18 mm, L/D of 17.8, compression ratio of 4, and helix angle 17.8°. No mixing devices were present. The barrel temperature was 240°C, and the mold temperature 30°C. The injection speed and pressure were 6.1 cm^3/s and 1500 bar, respectively. Tensile (ASTM D-638 type IV) and impact (ASTM D-256) specimens were obtained.

Filled blends were obtained by a two-step process. In the first step, phenoxy pellets and the filler were mixed in a single-screw extruder up to 50/50 ratio, which was the maximum filler content consistent with adequate mixing. This limited the maximum PA 6 content of the blends to approximately 60% in weight in the case of 30% filler and to 75% in the case of 20% filler. The diameter, L/D, and compression ratio of the screw of the extruder (BRABENDER) were 19 mm, 25, and 2/1, respectively. A six elements kenics static mixer was used between the extruder and the die to improve the mixing efficiency. At the exit of the cylindric die, the material was pelletized and then tumbled with the PA 6 and phenoxy pellets to obtain the filled blends. The blends are identified by three numbers that indicate the weight content of PA 6/phenoxy/filler of the composite, respectively. The molding conditions used and the specimens obtained were the same as those of the unfilled blends.

The phase behavior of the blends was studied by DSC using a Perkin–Elmer DSC-7 calorimeter at a heating rate of 20°C/min in a nitrogen atmosphere. Two heating scans were carried out between 15 and 260°C. Cooling between both scans was carried out at the maximum rate provided by the calorimeter. Given the worse accuracy of the results of the first scan, the reported thermal transitions and the melting heats of PA 6 were those determined in the second scan in the usual way.

Tensile testing was carried out on an Instron 4301 tester at 23 ± 2°C on 2-mm thick ASTM D-638 type IV specimens. A crosshead speed of 20 mm/min was used. The mechanical properties [Young's modulus (E), yield stress (σ_y), break stress and strain (σ_b and ε_b, respectively)] were determined from the force-displacement curves. Izod impact tests were carried out on 3-mm thick notched specimens using a CEAST 6548/000 pendulum. The notch (depth 2.54 mm) was machined after injection molding, and, because of the low values obtained with the standard radius (0.25 mm), close to the detection limit of the apparatus, a wider notch tip radius was employed (1 mm). A minimum of eight and five specimens were tested for each determination of tensile and impact tests, respectively. Scanning electron microscopy (HITACHI S-2700) was carried out after gold coating on cryogenically, tensile, and impact-fractured surfaces at an accelerating voltage of 15 kV.

RESULTS AND DISCUSSION

Phase Structure

When the calorimetric scans of the filled blends were performed, two T_gs were observed whatever the composition. The low temperature T_g at approximately 42°C, which corresponded to the PA 6 amorphous phase, did not change with composition. This indicated the presence of a practically pure PA 6 phase, irrespective of the blend composition. The high temperature T_g of pure phenoxy at approximately 87°C, showed a slight shift ($\approx$12°C) to lower temperatures as the PA 6 content in the blend increased, which was confirmed by dynamic-mechanical thermal analysis (DMTA) measurements. Taking into account the lack of significant presence of low molecular weight products mentioned by the producer, this indicated a slight presence of PA 6 in the phenoxy phase.

This T_g behavior was very similar to that seen in the unfilled blends.[35] However, in a PA 66/PP

Figure 1 Heat of fusion of mica- and calcium carbonate-filled blends against PA 6 content; (○) unfilled blends, (□) 10% weight filled blends; (◇) 20% filled blends; and (△) 30% filled blends.

blend filled with glass beads,[6] increases in the T_g of PA 66 were observed when it was the minority component. This was related to morphology, because the glass beads seemed preferentially sorrounded by PA 66. In other works,[14,27] it was attributed to the PA 66/glass beads boundary-induced mobility decrease in the PA chains and subsequent T_g increase. In fact, shifts of relaxation spectra to higher temperatures,[36,37] but also to lower T_gs,[38] with the addition of fillers to pure polymers have been obtained. In the PA 6/phenoxy filled blends of this article, the lack of T_g change indicates a low interaction level. Moreover, it agrees, as seen later, with the fact that mineral particles were not preferentially surrounded by any of the blend components. This would make unlikely a possible change in the mobility of the chains and, as a consequence, in the T_g values.

With respect to melting and crystallization, the T_m of the PA 6 crystalline phase remained practically constant with blend composition. The heats of fusion of the PA 6 crystalline phase in both filled systems are shown in Figure 1. As can be seen, in these blends, no significant deviations of melting heat from linearity was observed. The appearance of a nucleating effect of mineral particles is not unusual in filled crystalline thermoplastics.[25,39–41] This behavior of the T_m and the heat of fusion indicated that the crystallization of PA 6 was not practically affected by the presence of either phenoxy or mineral fillers.

However, when the DSC scans of pure and filled PA 6, which are partially shown in Figure 2

Figure 2 Melting endotherms of unfilled and 10, 20, and 30% mica-filled PA 6.

in the case of mica filler, were performed, a low temperature shoulder appeared in the single PA 6 melting endotherm. It became almost as clear as the main peak detected when the mineral filler/PA 6 ratio increased. The appearance and increasing presence of the low-temperature endotherm in filled blends indicated that the crystalline nature of PA 6 was disturbed in the vicinity of the filler. This was also observed in other semicrystalline-filled thermoplastics,[15,42] in which the appearance of shoulders in the melting peaks was attributed to morphological changes at the polymer/filler interface. However, in some crystalline thermoplastics, including PA 6,[43-45] a melting–recrystallization process may take place during the heating DSC scan. This should give rise to a multiple melting behavior, with a low-temperature endotherm corresponding to melting of crystals grown by primary crystallization and a high-temperature endotherm of crystals formed through recrystallization. The low-temperature endotherm should become weaker as the recrystallization and the associated exotherm proceeds. This exotherm process may even cancel the endotherm associated with the first melting, and, as a consequence, a single peak, as seen in Figure 2 in the case of pure PA 6, may appear.

Recrystallization is favored by a low heating rate. As a consequence, at high heating rates, the tendency is to see more clearly the low-temperature endotherm.[43,44] For this reason, with the aim of verifying the possibility of recrystallization as the origin of the shoulder, calorimetric scans at different heating rates were performed in both filled blends. The low-temperature shoulder presence clearly grew as the heating rate increased. This behavior indicated that recrystallization hindered by the presence of filler was responsible

for the observed multiple melting. Perhaps because of the similar particle size seen later, the effect was not a function of the nature of the filler and was dependent only on the filler content. The comparison of the size of the deconvoluted peak attributable to melting of the primary crystallized PA 6 and that consequence of recrystallization, indicated that, after the scan, the amount of primarily crystallized and recrystallized PA 6 was similar in blends with 30% of filler and that the presence of primarily crystallized PA 6 increases as the amount of filler increases. Only recrystallized PA 6 should be present in unfilled blends.

In summary, DSC data show that, besides a crystalline phase, the filled blends are composed of two amorphous phases: a pure PA 6 phase and an almost pure phenoxy phase with slight PA 6 presence. Moreover, a nucleating effect of mineral fillers on PA 6 is not present. Finally, the mineral particles hinder the recrystallization of PA 6. Thus, although PA 6 was able to fully recrystallize in unfilled blends, in the case of 30% filled blends only approximately half of the PA 6 was able to recrystallize.

Morphology

The surfaces of the cryogenically fractured 60/20/20 (mica) and 40/40/20 and 20/60/20 (calcium carbonate) tensile specimens are shown in Figures 3(a–c), respectively. The morphology of the blend matrix was independent of the nature of the filler. The size of the dispersed phase of the blends was large (typically, 0.5–1 μm), both when PA 6 was the matrix and when it was the dispersed phase, and similar to that of unfilled blends.[35] A slight tendency to co-continuity appeared as the phenoxy content approached the phase-inversion composition (roughly 32/68). In the case of the impact specimens, the dispersed phase size was larger than that of the tensile specimens (roughly 50 to 100% larger) throughout the composition range. This was probably caused by the larger time for the dispersed phase to coalesce in the thicker impact specimens.

As can be seen, mixing was homogeneous, and the fillers were not preferentially sorrounded by either component of the blend. However, a heterogeneous distribution of the filler between the components of the blend in filled incompatible polymers blends is not unusual.[4-8,28] In fact, in PA 6 and PA 66 blends with PP filled with glass beads or fibers,[5,6,28] the filler appeared encapsulated by the polyamide at sufficient PA 6 or 66 content when the PP was the matrix, this being

(a)

(b)

(c)

Figure 3 (a) Cryogenically fractured tensile specimen of mica-filled 60/20/20 composition; (b) tensile-fractured calcium carbonate filled 40/40/20 composition; and (c) tensile-fractured calcium carbonate filled 20/60/20 composition.

independent of the mixing sequence. This behavior was attributed to a difference in polarity, which induced a different affinity of the filler for each component. In the case of the PA 6/phenoxy blends of this article, the lack of preferential location of the fillers agrees with the presence of polar functional groups in the structure of both components of the blend.

As can also be observed in Figure 3(a), the planar shape of the mica particles was oriented during injection molding parallel to the flow. This particle orientation of planar fillers,[13,46,47] is a common result that, as seen in Figures 3(b) and (c), did not appear in calcium carbonate particles because of their irregular, more spherical, shape. In addition, the size distribution of the mica particles was wider (typically from 3 to 20 μm) than that of calcium carbonate (typically from 3 to 8 μm).

In Figures 4(a) and (b), a detail of the debonded mica and calcium carbonate interphase is shown. As can be seen, in mica-filled blends [Figure 4(a)], although some particles appeared broken, most of them appeared debonded from the matrix, with large voids sorrounding the particles, indicating lack of adhesion. Similar morphologies have been observed in mica/polypropylene composites.[48,49] In the case of calcium carbonate-filled blends [Fig. 4(b)], the particles were seen in the ductile zones, but in the case of brittle fracture, they were only seen when the fracture plane changed abruptly. Moreover, even after fracture, debonding was not complete. This fact indicated cohesive fracture and that adhesion in the calcium carbonate blends was good enough to avoid fracture through the interphase.

Mechanical Behavior

The Young's moduli of mica and calcium carbonate-filled PA 6/phenoxy blends, are shown in Figures 5(a) and (b), respectively, as a function of the thermoplastic composition. As can be seen, the reinforcing effect of both mica and calcium carbonate in the blends was important. This was because, in the case of a 10% filler content, the increase in modulus, measured as the mean distance in modulus between the 0 and 10% filler compositions [1000 MPa and 700 MPa, respectively in Figs. 5(a) and (b)], is roughly 35 and 25% of the value of the unfilled matrix, respectively, for mica and calcium carbonate composites. The higher reinforcing ability of mica was probably because flake materials such as mica, because of their large aspect ratio,[3] produce large increases

(a)

(b)

Figure 4 Detail of the interphase of: (a) 40/40/20 mica; and (b) 20/60/20 calcium carbonate tensile-fractured specimens.

in modulus, especially if they are oriented predominantly in one plane,[3,50–52] as was seen to take place in these blends in Figure 3(a).

As can also be seen, in the case of mica filling, the reinforcing effect on the blends was similar to that which takes place in the case of pure components. This indicates that the affinities of mica for PA 6 and phenoxy are similar. However, in the case of calcium carbonate, as seen in Figure 5(b), the reinforcing effect was higher in the case of the blends than in the case of the pure components and positive deviations were observed. This indicates that the positive effect of the filler on the moduli of the blends was larger than that on the pure components.

When the Tsai–Halpin model[53] (eq. 1)

$$E_c = E_m \frac{1 + n \phi \varphi}{1 - n \phi} \quad n = \frac{(E_f/E_m) - 1}{(E_f/E_m) + \varphi} \quad (1)$$

where E_c, E_m, and E_f are the composite, matrix, and filler modulus, respectively, ϕ is the filler volume fraction, and φ is an adjustable parameter that has been related to reinforcement geometry, packing geometry, and loading conditions, was applied to the mica filled 50/50 blend, the behavior was in the middle between those of filled PA 6 and filled phenoxy. The different behavior of the moduli of calcium carbonate-filled PA 6, phenoxy, and 50/50 blend against filler content is seen in Figure 6, where the moduli values are approximated to the Tsai–Halpin model. As can be seen, the modulus values of the filled 50/50 blend were the same as those of the PA 6, which were the upper limit. This clearly indicated the improved effect on the blends of the calcium carbonate as compared to that of the two pure components. This behavior may be related to the adhesion between filler and matrix, because in thermoplas-

Figure 5 Young's modulus of unfilled and filled: (a) mica; and (b) calcium carbonate composites against phenoxy content in the thermoplastic phase; symbols as in Figure 1.

Figure 6 Young's modulus against calcium carbonate volume content in the case of PA 6 (○), phenoxy (□) and 50/50 matrixes (◇); the continuous line indicates the values obtained from the Tsai–Halpin model.

tics modified with fillers,[54,55] small-strain mechanical properties may be influenced by interfacial adhesion. As was mentioned above, adhesion seemed to be better in calcium carbonate-filled blends than in mica-filled ones, as observed by SEM.

Figures 7(a) and (b) show the yield stress values obtained for mica- and calcium carbonate-filled blends, respectively. The numbers in parentheses indicate the number of specimens that broke after yielding. The value is not shown when all the specimens yielded. When yielding was not attained in some mica-filled composites, the corresponding break stress was plotted as a filled symbol. As can be seen, in both fillers, the positive effect on yield stress of the filler presence was higher than that which could be expected from the effects observed in the two filled pure polymers. In filled thermoplastics, continuous decreases[49,56] but also slight maximums at low filler contents,[48,57] and when adhesion is sufficient, yield stress increases with filler content[56,58] have been found. In the case of mica-filled PP, yield stress decreases were obtained in untreated composites; whereas, the behavior improved when a coupling agent was added.[49]

If we look at the overall behavior of both filled and unfilled blends with respect to composition in Figure 7, they seem similar. This seems to indicate that in the case of these composites with a blend matrix, these positive deviations seem to be more attributable to the positive deviations proper to the unfilled blends than to the presence of fillers. However, the synergisms of Figure 7 seem to be larger in the filled blends than in the unfilled ones. For this reason, the experimental

values of the filled 50/50 blend and of pure polymers were fitted to the power law of Nicolais et al.[59] and the exponential law of Pukanszky.[60] The last one:

$$\sigma_{yc} = \sigma_{ym} \frac{1 - \phi}{1 + 2.5\phi} \exp(B\phi) \qquad (2)$$

where σ_{yc} and σ_{ym} are the yield stresses of the composite and the matrix respectively, ϕ is the volume fraction of filler, and B is a parameter characterizing the interaction between matrix and filler, showed the better and a good fit to the experimental values. The calculated values of B are shown in Table II for the 50/50 blend and the pure polymers as a reference. As can be seen, the beneficial effect of the presence of fillers is larger in the blends than in the pure polymers. This was because B at least equals the increase in yield stress of the best of the two components. This can be attributed to the fact that the large particles are in contact with the two components, and, as a consequence, debonding will occur only when the

Figure 7 Yield stress of unfilled and (a) mica- and (b) calcium carbonate-filled blends against phenoxy content in the thermoplastic phase; symbols as in Figure 1.

Table II   Values of the B Parameter of the Pukanszky Model for Yield Stress

Filler Matrix	Mica			Calcium Carbonate		
	PA 6	Phenoxy	50/50	PA 6	Phenoxy	50/50
B	5.07	4.40	5.16	4.16	3.94	4.16

stress and strain level of the best performing component are overcome.

Figures 8(a) and (b) show the ductility values of mica- and calcium carbonate-filled blends, respectively. As is known, adhesion in filled untreated polymers is not usually good enough at large strains, and debonding usually occurs, leading to premature failure[46,48,54] with respect to that of the unfilled polymer. Poor adhesion and its relation with mechanical properties has been described in mica-reinforced thermoplastics without coupling agents.[49,55] This was the reason for the important ductility decrease observed in Figures 8(a) and (b), even with only 10% in weight of filler

Figure 8 Ductility of unfilled and (a) mica- and (b) calcium carbonate-filled blends against phenoxy content in thermoplastic phase; symbols as in Figure 1.

(roughly 4% in volume). As can also be seen, the ductility of filled PA 6 is smaller than that of filled phenoxy, despite the higher elongation at break of neat PA 6. This large sensitivity of the ductility of PA 6 to filler presence has been seen both in unmodified and coupling agents[24] modified PA 6. The ductility of the calcium carbonate-filled blends was higher than that of mica composites. This was probably because of the sharp edges of mica particles that promote cracks and to the higher adhesion of calcium carbonate composites.

When the effect of the fillers on the blends are compared with those on the pure components, we realize that the positive, or in the case of ductility, less negative, effect of the filler on the properties of the blends also takes place. This is because, although a less detrimental effect in the case of ductility did not appear in mica-filled composites, it took place in the case of ductility of calcium carbonate-filled composites up to a filler content between 10 and 20%. The slightly better adhesion in the blends will probably account for the observed difference.

The impact strength of filled blends is shown in Figures 9(a) and (b). As can be seen, the negative effect of the presence of filler on the impact strength of the blends was smaller than that which took place when the pure polymers were filled. This took place mainly at high filler contents and in calcium carbonate-filled systems.

Although maxima in the impact strength of composites have been observed at low or intermediate filler contents both in untreated[48] and treated composites,[49,54,61] impact strength decreases in filled composites with respect to those of unfilled polymers is the usual behavior, as has been observed in calcium carbonate and calcium silicate/PA 6[24] and glass beads/PA 6 composites.[62] This fragility of the blends observed in impact tests agrees with the sharp ductility decrease observed upon the addition of only 10% of filler and may be related to the fact that PA 6 is known to be a notch-sensitive material,[63] in which sharp edges and stress concentrations induced by the very different nature of the components act as

Figure 9 Impact strength of unfilled and (a) mica- and (b) calcium carbonate-filled blends against phenoxy content in the thermoplastic phase; symbols as in Figure 1.

notches, giving rise to decreases in ductility and impact strength.

CONCLUSIONS

Neither mica nor calcium carbonate particles affected the solid-state structure and morphology of the almost completely immiscible PA 6/phenoxy blends, with the exception of multiple melting in PA 6, probably because of a filler-hindered recrystallization process.

The reinforcement of the Young's modulus and yield stress of the blends caused by the presence of filler was comparatively higher than that which took place in the case of the pure components, mainly in the case of calcium carbonate. Less negative influence of the filler presence on the break properties of the blends was also obtained with calcium carbonate. The inevitable contact of the fillers with the better adhered component may play a role in the observed mechanical be-

havior, together with the ability of mica particles to promote cracks and the better adhesion between calcium carbonate particles and the matrix.

REFERENCES

1. Favis, B. D.; Therrien, D. Polymer 1991, 32, 1474.
2. Chen, C.; Fontan, E.; Min, K.; White, J. L. Pol Eng Sci 1988, 28, 69.
3. Lusis, J.; Woodhams, R. T.; Xanthos, M. Polym Eng Sci 1973, 13, 139.
4. Stamhuis, J. E. Polym Comp 1988, 9, 72.
5. Benderly, D.; Siegmann, A.; Narkis, M. J Mater Sci, Lett 1995, 14, 132.
6. Ulrich, M.; Caze, C.; Laroche, P. J Appl Polym Sci 1998, 67, 201.
7. Asai, S.; Sakata, K.; Sumita, M.; Miyasaka, M. Polym J 1992, 24, 415.
8. Mitsuishi, K.; Kodama, S.; Kawasaki, H. Polym Comp 1988, 9, 112.
9. Scott, C.; Ishida, H.; Maurer, F. H. J. Polym Comp 1992, 13, 237.
10. Chiang, W.; Yang, W.; Pukanszky, B. Polym Eng Sci 1992, 32, 641.
11. Zhang, H.; Berglund, L. Polym Eng Sci 1993, 33, 100.
12. Avalos, F. J Polym Eng 1991, 10, 253.
13. Arroyo, V. M.; Vigo Matheu, J. P. Rev Past Modernos 1987, 374, 217.
14. Scherbakoff, N.; Ishida, H. Makromol Chem, Macromol Symp 1993, 70/71, 459.
15. Morales, E.; Herrero, C. R.; Acosta, J. L. Polym Bull 1991, 25, 391.
16. Kayano, Y.; Keskkula, H.; Paul, D. R. Polymer 1997, 38, 1885.
17. Lee, J. D.; Yang, S. M. Polym Eng Sci 1995, 35, 1821.
18. Armat, R.; Moet, A. Polymer 1993, 34, 977.
19. Eguiazábal, J. I.; Nazábal, J. Plast Rubb Process Appl 1990, 14, 211.
20. Horiuchi, S.; Matcharivakul, N.; Yase, K.; Kitano, T.; Choi, H. K.; Lee, V. M. Polymer 1997, 38, 59.
21. Ahn, T. O.; Hong, S. C.; Jeong, H. M.; Kim, J. H. Polymer 1997, 38, 207.
22. Gattiglia, E.; Turturro, A.; La Mantia, F. P.; Valenza, A. J Appl Polym Sci 1992, 46, 1887.
23. Murthy, N. S.; Kotliar, A. M.; Sibilia, J. P.; Sacks, W. J Appl Polym Sci 1986, 31, 2569.
24. Luo, H.; Han, C.; Mijovic, J. J Appl Polym Sci 1983, 28, 3387.
25. Cheshkov, V.; Natova, M.; Ashurov, N.; Usmanova, M.; Vekselman, A. J Appl Polym Sci 1997, 64, 1255.
26. Meddad, A.; Fisa, B. J Appl Polym Sci 1997, 65, 2013.

27. Ishida, H.; Scherbakoff, N. Makromol Chem Macromol Symp 1991, 50, 157.

28. Benderly, D.; Siegmann, A.; Narkis, M. Polym Comp 1996, 17, 86.

29. Porter, R. S.; Wang, L. H. Polymer 1992, 33, 2019.

30. Martínez, J. M.; Eguiazábal, J. I.; Nazábal, J. J Macromol Sci-Phys 1991, B30, 345.

31. Defieuw, G.; Groeninckx, G.; Reynaers, H. Polymer 1989, 30, 2164.

32. Iriarte, M.; Espi, E.; Etxeberria, A.; Valero, M.; Fernández, M. J.; Iruin, J. J. Macromolecules 1991, 24, 5546.

33. Eguiazábal, J. I.; Iruin, J. J. Mat Chem Phys 1987, 18, 147.

34. Erro, R.; Gaztelumendi, M.; Nazábal, J. J Polym Sci, Polym Phys Ed 1996, 34, 1055.

35. Guerrica-Echevarría, G.; Eguiazábal, J. I.; Nazábal, J. J Appl Polym Sci, to appear.

36. Nielsen, L. E.; Landel, R. F. Mechanical Properties of Polymers and Composites. II; Marcel Dekker: New York, 1994; 425.

37. Beaty, C. L. Polym Comp 1984, 5, 319.

38. Linares, A.; Morales, E.; Ojeda, M. C.; Acosta, J. L. Angew Makromol Chem 1987, 147, 41.

39. Liu, Z.; Gilbert, M. J Appl Polym Sci 1996, 59, 1087.

40. Velasco, J. I.; de Saja, J. A.; Martinez, A. B. J Appl Polym Sci 1996, 61, 125.

41. Fujiyama, M.; Wakino, T. J Appl Polym Sci 1991, 42, 2739.

42. Acosta, J. L.; Ojeda, M. C.; Morales, E.; Linares, A. J Appl Polym Sci 1986, 31, 1869.

43. Eguiazábal, J. I.; Cortázar, M.; Iruin, J. J. J Appl Polym Sci 1991, 42, 489.

44. Cortázar, M.; Iruin, J. J.; Eguiazábal, J. I. Polym Bull 1992, 29, 415.

45. Wunderlich, B. Macromolecular Physics, Vol. 3: Crystal Melting; Academic: New York, 1980; p 186.

46. Guerrica-Echevarría, G.; Eguiazábal, J. I.; Nazábal, J. Eur Polym J. 1998, 34, 1293.

47. Fujiyama, M.; Wakino, T. J Appl Polym Sci 1991, 43, 97.

48. Vu-Khanh, T.; Sanschagrin, B.; Fisa, B. Polym Comp 1985, 6, 249.

49. Bajaj, P.; Jha, N. K.; Jha, R. K. Polym Eng Sci 1989, 29, 557.

50. Newman, S.; Meyer, F. J. Polym Comp 1980, 1, 37.

51. Rexer, J.; Anderson, E. Polym Eng Sci 1979, 19, 1.

52. Maine, F. W.; Sheperd, P. D. Composites 1974, 5, 193.

53. Halpin, J. C.; Kardos, J. L. Polym Eng Sci 1976, 16, 344.

54. Maiti, S. N.; Mahapatro, P. K. J Appl Polym Sci 1991, 42, 3101.

55. Tausz, S.; Chaffey, C. J Appl Polym Sci 1982, 27, 4493.

56. Jancar, J.; Dianselmo, A.; Dibenedetto, A. T. Polym Eng Sci 1992, 32, 1394.

57. Katz, H. S.; Milewski, J. V. Handbook of Fillers for Plastics; Van Nostrand Reinhold: New York, 1987; p 225.

58. Jancar, J.; Kucera, J. Polym Eng Sci 1990, 30, 714.

59. Nicolais, L.; Narkis, M. Polym Eng Sci 1971, 11, 194.

60. Pukanszky, B.; Turcsanyi, B.; Tudos, F. in Interfaces in Polymer, Ceramic, and Metal Matrix Composites, Ishida, H.; Ed.; Elsevier: New York, 1988; p 467.

61. Sharma, Y. N.; Patel, R. D.; Dhimmer, I. H.; Bhardwaj, I. S. J Appl Polym Sci 1982, 27, 97.

62. Nijenhuis, K.; Addink, R.; van der Vegt, A. K. Polym Bull 1989, 21, 467.

63. Vincent, P. I. Impact Tests and Service Performance of Thermoplastics; Plastics Institute: London, 1971; p 36.